NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report 32-1204

Fabrication and Characterization of Hot-Pressed Tantalum Carbide

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Abstract

The microstructure and chemistry of a series of compacts of tantalum carbide hot-pressed from several commercially available powders were studied. Variations in behavior of the powders were observed during hot-pressing. These variations did not correlate with measured characteristics of the material. Densification did not appear to be a diffusion-controlled process; some evidence points to plastic deformation as a possible controlling process. Grain growth rates during pressing were 42 or 165 kcal/g mole, depending on the source of powder. The difference was not explained. An impurity grain boundary phase of Ta_2O_5 was observed as were variations in the tantalum/carbon ratio within a given compact.

Fabrication and Characterization of Hot-Pressed Tantalum Carbide

I. Introduction

Tantalum carbide (TaC) has a high melting point of approximately 4000°C (Ref. 1). This material exhibits little atomic mobility at temperatures in the order of 2000°C and, therefore, should be a useful structural material for applications up to this temperature. However, the behavior of available polycrystalline carbides, at low or high temperatures, is relatively unknown. For example, the strength-versus-grain-size relationship is undetermined. As part of a program to prepare tantalum carbide mechanical test specimens, techniques were developed for fabrication and evaluation of the character of the fabricated pieces. The refractory metal carbides (tantalum carbide included) are brittle at low temperatures and powder metallurgy techniques, such as hot-pressing, are convenient means of fabricating dense pieces of polycrystalline material (theoretical density of stoichiometric TaC is 14.45 g/cm³). These techniques were used and all results and discussion herein are concerned with such commercial powders prepared into polycrystalline specimens.

In many cases, the general results and conclusions are inferences drawn from observations rather than controlled experiments, because the primary goal of the effort was not to evaluate the character of the material, but to support a mechanical evaluation program. A substantial stock of TaC blocks ¾ in. in diameter and 2½ in. long was produced for mechanical testing. Results of these tests are reported in Ref. 2. However, because of the large quantity of information obtained concerning the chemistry and character of TaC and its usefulness to other investigators, this information is reported herein.

II. Materials

Three distinct grades of TaC were used in these studies, although subsequent processing and evaluation indicated that, to some extent, each lot of material within a given grade should be considered different. The basic grades used are listed in Table 1.

Table 1. Tantalum carbide powders

Type	Particle size, μ	C/Ta[d] ratio	O_2, wt %	Metallic, wt %	N_2, wt %	Free C, wt %	Unit cell, Å
Cerac[a]	5	0.99	0.05	<0.04	0.01	0.08	4.456
Ciba[b] 100	0.01	Not determined	1.7	<0.04	Not determined	0.6	4.455
Ciba[c] 1000	0.1	0.92—0.98	0.16—0.4	<0.03	0.03	0.04—0.3	4.444—4.453

[a]Single batch supplied by Cerac, Inc., Butler, Wisc.
[b]Single batch supplied by Ciba Corp., Summit, New Jersey.
[c]Mutiple batches supplied by Ciba Corp., Summit, New Jersey.
[d]Carbon to tantalum by chemical analysis.

A. Hot-Pressing Procedures and Equipment

All specimens described in this report were fabricated in a vacuum hot press of all-graphite construction. The unit operated in the 10^{-5} torr range to approximately 2000°C and the 10^{-4} torr range to approximately 2200°C. Inert gases could be used to 2500°C. A total radiation pyrometer regulating a silicon-controlled rectifier package was used for temperature control.

Pressings were conducted in dies approximately ¾ in. in diameter at pressures of up to 10,000 psi. Die cases were fabricated from Speer grade No. 3499S graphite.[1] Punches were made either from this material or from Poco grade No. P1924 graphite.[2] The latter showed less breakage at pressures above 6500 psi.

The most successful procedure for application of pressure and temperature was to maintain approximately 10% of the maximum pressure until a temperature of 1600°C was reached. At this point, the linear increase in pressure was applied until maximum temperature and pressure were attained. Temperature was also held constant at approximately 1350°C for 30 min to permit vacuum recovery, unless otherwise noted.

Specific gravities were determined by kerosene displacement and lattice parameters by a Nelson-Reilly computation from X-ray diffraction goniometer data. Metallography specimens were prepared by conventional polishing with a 50% nitric–50% HF solution used for grain boundary etching. Grain sizes were determined by Fullman's line-count technique.

Chemical analyses were obtained from various sources, either as a procured or subcontracted service. Microprobe

[1]Speer Carbon Co., St. Marys, Pa.
[2]Poco Graphite, Inc., Garland, Texas.

Table 2. Hot-pressing characteristics of Cerac TaC

Vacuum Hot Press No.	Temperature, °C	Pressure, kpsi	Time, h	Density, g/cm³	Grain size, μ	Powder jet-milled[c]	Degas[a]
20	2190	6.5	1.0	14.30	31	No	No
25	2015	6.5	2.5	13.77	26.5	Yes	No
31	2360	6.5	0.4	13.48	36.0	No	No
33	2420	6.5	0[b]	13.53	Not determined	No	No
34	1815	6.5	2.0	14.06	24	Yes	Yes
35	1915	6.5	1.7	13.84	Not determined	Yes	No
37	1815	6.5	1.0	13.92	Not determined	Yes	Yes
39	1915	6.5	1.4	14.06	Not determined	Yes	Yes
46	1710	6.5	1.5	14.03	15	Yes	Yes
47	2015	6.5	1.5	14.06	Not determined	Yes	Yes

[a]30-min hold at 1300—1400°C in place.
[b]Power loss caused termination of run.
[c]Power passed once through Jet Trost mill to reduce particle size to < 1μ.

analyses were conducted with an Applied Research Laboratory probe (model EMX) using a low element attachment.

B. Results

Many of the determined parameters for the starting powders are presented in Table 1 and, for the hot-pressed compacts, in Tables 2, 3, and 4. Typical microstructures of samples indicated are shown in Figs. 1 through 4. Pertinent chemical analyses are included in Tables 1 and 5. Extensive details of the nature of impurities are not listed because impurity analysis varied from sample to sample and from technique to technique.

C. Discussion

Table 4 illustrates that, when various lots of the same kind of powder were used, the pressing parameters required to obtain comparable densities varied from lot to lot of powder. It should be noted that specimen 40 was

Table 3. Hot-pressing characteristics of Ciba 100 TaC

Vacuum Hot Press No.	Temperature, °C	Pressure, kpsi	Time, h	Density, g/cm³	Grain size, μ
23	1260	8.	0.5	9.2	Not determined
27	1360	6.5	1.	11.2	Not determined
28	1460	6.5	1.4	12.4	2ᵃ
30	1715	6.5	2.	14.06	4ᵃ
41	1615	10.	0.7	14.5	3

ᵃEstimate.

Table 4. Hot-pressing characteristics of Ciba 1000 TaC

| Vacuum No.	Batch	Temperature, °C	Pressure, kpsi	Time, h	Density, g/cm³	Grain size, μ	
38	1-1	1610	6.5	2.0	14.06	6	
40	1-1	1710	6.5	1.3	14.44	10	
43	1-1	1510	6.5	1.5	12.04	Not determined	
44	1-1	1815	6.5	1.5	14.42	35	
50	1-1	1610	9.0	0.8	14.40	13	
51	1-1	1560	9.5	1.5	14.45	9	
85	2-1	1815	7.0	1.5	11.29	Not determined	
88	2-2	2115	8.0	1.3	13.65	8.3	
89	2-4	2015	8.0	0.6	14.46	29	
90	2-4	1815	8.0	0.5	12.35	Not determined	
91	2-4	1965	8.0	1.3	13.85	Not determined	
92	2-3	2015	8.0	0.5	14.35	10/250ᵃ,ᵇ	
94	2-5	2015	8.0	1.0	13.25	10	
100 A	3-1	1710	7.5	0.05	13.10	2	} two-part pressing
100 B	3-2	1710	7.5	0.05	13.60	Not determined	furnace failure limited time
105	2-5 + C	1915	7.0	0.5	12.71	1-2ᵃ	
106	3-3	1815	6.5	0.75	14.25	25	
133	4-1	2015	7.5	0.75	13.02	2ᵃ	

ᵃEstimate.
ᵇDuplex structure.
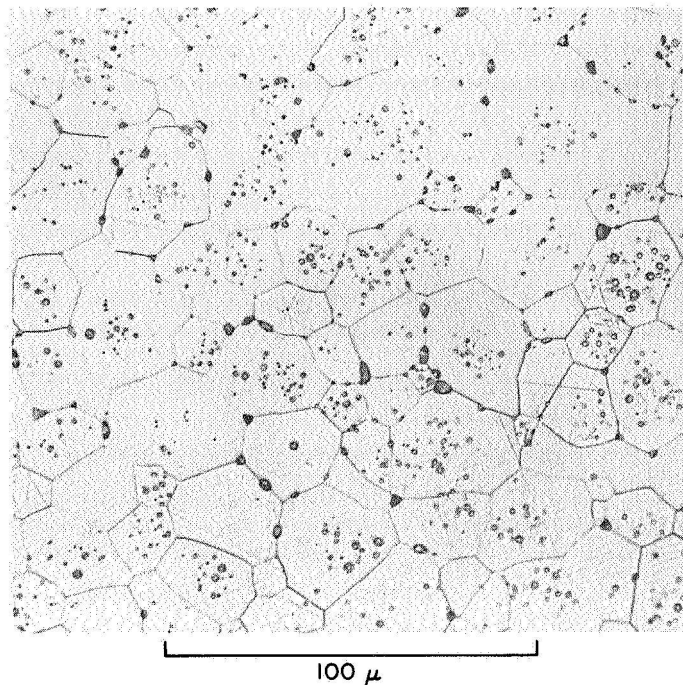
Fig. 1. Tantalum carbide, vacuum hot press 25 (Table 2), Cerac. Density: 13.77 g/cm³
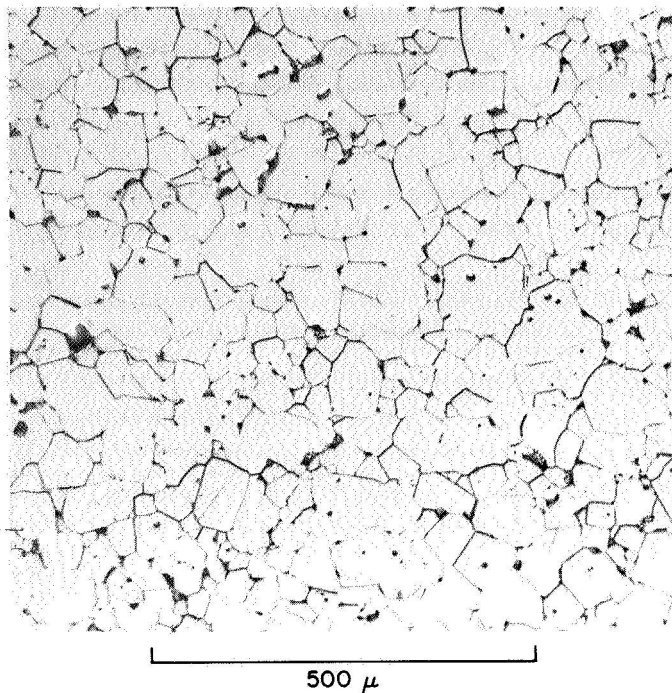

Fig. 3. Tantalum carbide, vacuum hot press 40 (Table 4), Ciba 1000. Density: 14.44 g/cm³ (high pressability)
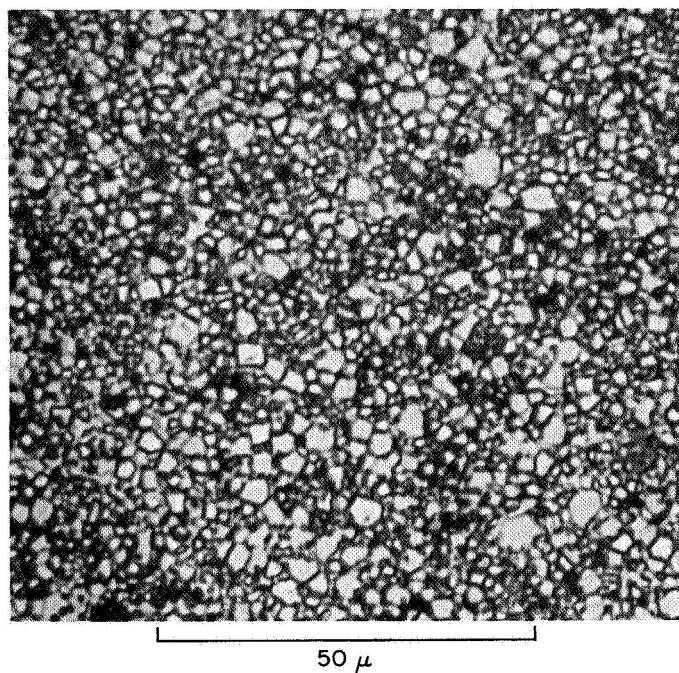

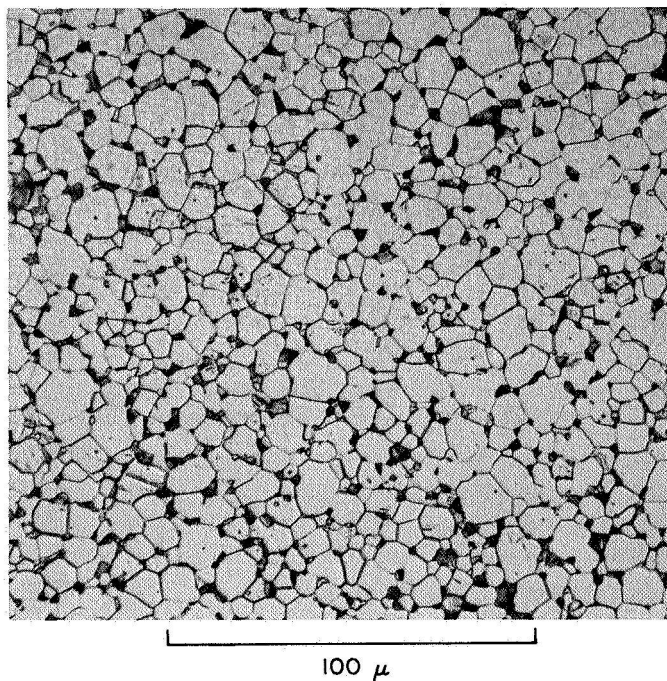Fig. 2. Tantalum carbide, vacuum hot press 30 (Table 3), Ciba 100. Density: 14.06 g/cm³

Fig. 4. Tantalum carbide, vacuum hot press 94 (Table 4), Ciba 1000. Density: 13.25 g/cm³ (low pressability)

Table 5. Characteristics of Ciba 1000 Å TaC

	As received powder						Pressing conditions			After hot pressing				
Batch[a]	Particle size,[b] Å	Lattice parameter,[b] Å	Free C, wt %	Total C, wt %	O_2, wt %	Other, wt %	Batch[a]	Temperature, °C	Pressure, kpsi	Density, g/cm³	Lattice parameter,[b] Å	Free C, wt %	Combined C, wt %	O_2, wt %
1-1	948	4.453	0.38[c]	6.28[c]	0.16[c]	<0.10[c]	1-1	1710	6.5	14.44	4.454	<0.01[d]	6.00[d]	0.3[d]
			0.33[d]	5.76[d]	0.56[d]			1610	6.5	14.07	4.454	<0.01[d]	5.93[d]	0.2[d]
			0.22[d]	6.33[d]	0.165[e]	0.07[e,f]		1815	6.5	14.42	4.452			
			0.15[d]	6.27[d]				1560	9.5	14.45	4.453			
								1710	6.5	14.00	4.448	0.02[c]	5.88[c]	0.01[c]
2-2	641	4.451	0.25[c]	5.95[c]	0.20[c]	0.01Cu[g]	2-2	2115	8.0	13.70	4.444	<0.01[d]	6.19[d]	0.07[d]
			0.14[d]	6.25[d]	0.075[e]	0.01Zr[g]		1865	7.0	12.35	4.449		5.60[c]	0.02[c]
2-3	537	4.451	0.30[c]	6.00[c]	0.28[c]	<0.10[c]	2-3	2015	8.0	14.35	4.447			
			0.16[d]	6.27[d]	0.028[e]			1915	6.5	14.39		0.07[c]	5.81[e]	<0.01
2-4	452	4.451	0.30[c]	6.00[c]	0.28[c]	0.01Cu[g]	2-4	2015	8.0	14.65				
			0.084[d]	6.21[d]		0.01Zr[g]		1965	8.0	13.85	4.448	0.04	5.82[c]	<0.01[c]
					0.05[e]	0.04[g]		1815	8.0	12.40	4.448			
2-5	452	4.448	0.23[c]	5.93[c]	0.23[c]	<0.10[c]	2-5	2015	8.0	13.25	4.446	0.1[c]	5.74[c]	0.01[c]
			0.043[d]	6.20[d]	0.45[e]			1915[i]	6.5[i]	13.40[i]		0.01[c]	5.64[c]	0.01[c]
3-1	527	4.444	0.27[c]	5.95[c]	0.35[c]		3-1	1660[h]	7.5[h]	13.10[h]		0.01[c]	5.85[c]	0.02[c]
		4.447			0.18[e]									
3-2	539	4.452	0.31[c]	6.00[c]	0.18[c]		3-2	1660[h]	7.5[h]	13.60[h]				
		4.449			0.22[e]	<0.15[g]		1915[i]	6.5[i]	14.30[i]		0.02[c]	5.75[c]	<0.01[c]
3-3	415	4.449	0.30[c]	6.00[c]	0.30[c]		3-3	1815	6.5	14.25		0.03[c]	5.64	0.02
					0.55[e]			1916[i]	6.5[i]	14.72[i]	4.446	0.02[c]	5.75[c]	<0.01[c]
3-4	330	4.453	0.40[c]	6.00[c]	0.23[c]		3-4	1815	6.5	14.38	4.452	0.01[c]	5.89[c]	0.03[c]
					0.018[e]									
4-1		4.455	1.0[c]	6.60[c]	0.5[c]		4-1	2015	7.5	13.02	4.455			

[a]First number is purchase order, second is partial shipment.
[b]Determined by X-ray diffraction at JPL.
[c]Determined by Ciba.
[d]Determined by National Spectrographic Laboratories.
[e]Determined by Sperry Rand Research Center.
[f]Nb-1, Ni-5, Cu-15, Fe-90, Ca-10, Al-12, Si-5, P-1, S-25, Cl-25, K-1, Ti-3, Cr-10, Mn-2 ppma.
[g]Determined by Pacific Spectrochemical Laboratory, metallics.
[h]Ram broke at this temperature and pressure; pressing was incomplete.
[i]Refers to total metallic impurities, unless otherwise specified.

theoretically dense at 6500 psi and 1715°C, while specimens 85 and 90 obtained less than 90% of density under higher temperatures and pressures. The grain sizes and porosities shown in Figs. 3 and 4 are consistent with this difference in pressability. Careful evaluation of the characteristics of the starting powders did not reveal any differences that could be directly correlated with this difference in behavior. The characteristics evaluated included particle size and shape by electron microscopy, particle size by X-ray line broadening, X-ray lattice spacing, and total or specific impurity levels. Table 5 presents a summary of characteristics of the powders before and after pressing. Although variations existed among the various lots before and after pressing, lack of precision of the measurements (especially for chemical analysis) and lack of consistent trends preclude any clear

dependency. The only correlation noted, which was sub-
ject to exceptions, appeared to be with the final C/Ta
ratio in the compact, as determined by unit cell measure-
ment. This ratio may be different from the initial starting
powder because of (1) removal of carbon by reaction
with the oxygen present to form volatile CO, and (2) ad-
dition of carbon from the graphite components during
pressing. The former process is believed to be consider-
ably more active at the temperatures discussed herein.
Oxygen is not believed to aid densification because
Lot 1-1 of powder was comparable to the other lots with
respect to oxygen, but was, by far, the easiest lot to
hot-press.

Figure 5 also shows the effect of C/Ta ratio on the
densification. This figure is an example of poorly densi-
fying material (Lot 2-5) to which carbon flakes were
added in an attempt to increase the C/Ta ratio. The
temperature was insufficient to homogenize the sample;
however, the density and grain-size gradient surrounding
the carbon flakes appear to support the postulate that
increased C/Ta ratio enhances sinterability.

Unfortunately, attempts to fabricate a special lot of
carbon-rich TaC (Lot 4-1) did not back up this hypothe-
sis. Pressing No. 133 is typical, obtaining only 90% of
density at 2015°C. However, here again, two different
basic lots of powder are being compared and may have
differences other than C/Ta ratio. Hence, it must be
concluded that the C/Ta ratio is only one factor con-
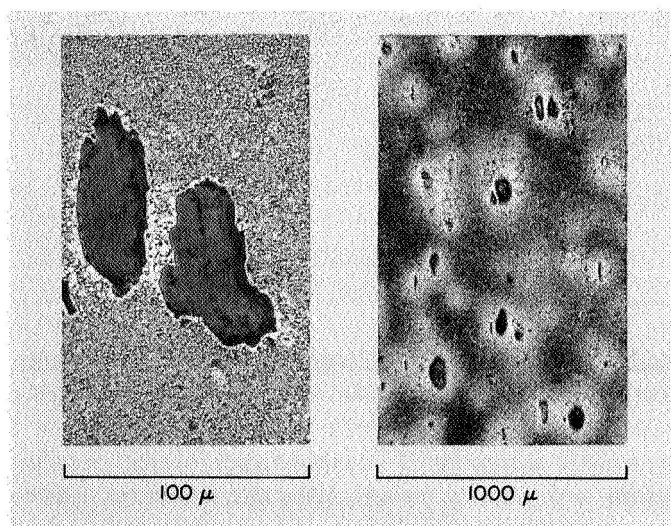trolling the densification of TaC.

**Fig. 5. Tantalum carbide, vacuum hot press 105 (Table 4),
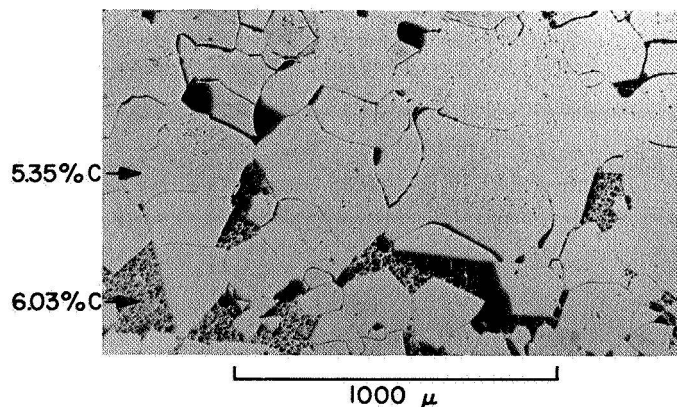Ciba 1000 + 0.5 weight percent C. Density: 12.71 g/cm³**

**Fig. 6. Tantalum carbide, vacuum hot press 92 (Table 4),
Ciba 1000. Density: 14.35 g/cm³**

Figure 6 illustrates the existence of nonhomogeneity.
The C/Ta ratios indicated were determined by electron
beam microprobe analysis and were standardized against
a piece of dense TaC for which the C/Ta ratio had been
repeatedly determined. Standardization against pure
tantalum and pure carbon was inaccurate because of the
differences in X-ray absorption of the samples in the mi-
croprobe. Consequently, although the absolute values of
C/Ta ratio are perhaps no better than ±10%, the rela-
tive values should be within ±3%. The cause of this
difference in behavior within a given compact is not
clear. The powder was from a single lot and it can only
be summarized that such variations in composition
existed within this lot.

If the homogenization of the TaC is diffusion-
controlled, then, according to Ref. 3, temperatures of
1600 to 2100°C allow considerably less than 1-μ random
walk diffusion motion for carbon. (Random walk is ap-
plied because the composition gradients are small.) The
motion of tantalum is near two orders of magnitude
slower (Ref. 3) at 2500°C, and, if the mobilities remain
comparable with changes in temperatures, the motion of
Ta in TaC is negligible at these temperatures.

Further comparison of the densification behavior with
the available diffusion data provides two pertinent fac-
tors. Firstly, if the densification is diffusion-controlled,
then the carbon-deficient material should densify more
readily because it exhibits the higher diffusion constants.
However, the opposite relationship was observed. Sec-
ondly, the mobility of the carbon is one to two orders of
magnitude too low to permit Nabaro-Herring creep to
account for the deformation. The slower moving and
likely controlling tantalum is almost two orders of mag-
nitude slower at 2500°C, and again, if the mobilities

remain comparable at lower temperatures, then it is even more difficult for lattice diffusion to account for observed compaction. Surface and grain boundary diffusion may be involved; however, it has been suggested that grain boundary diffusion is not significant (Ref. 3) in TaC. These factors, the effect of carbon content, and total mobility suggest that another mechanism must be involved in the hot densification of TaC.

Plastic deformation, as a result of dislocation mobility, may be a possibility; however, data are not available for TaC. Dislocation motion is suggested in Ref. 4 to explain compressive creep behavior of TiC that did not appear diffusion-controlled. Figure 6 shows a stress effect with higher grain growth rates and higher pressing pressures. The possibility of a large stress dependence of the diffusion rate cannot be excluded; however,

a change of several orders of magnitude in diffusion rates with stress seems unlikely.

The rate of grain growth during hot pressing also provided a possible approach to the processes occurring during densification (Fig. 7). Because these data are final grain sizes obtained from compacts containing significant porosity during most of the growth, and because densification and, probably, deformation occurred during the growth, the numbers should be considered only relative. However, since these effects are reasonably constant, some indication of the mechanism should be obtainable.

The most apparent factor in Fig. 7 is the different rates of growth for the Cerac and Ciba 1000 TaC. The activation energies do not correspond with reported values for processes in TaC, but the energy for the motion of the slower moving and, therefore, controlling Ta in TaC, is apparently not available. The reason for these differences in behavior between the two types of TaC is not apparent because the compositions are comparable, with the exception of O_2. The primary difference, approximately 0.5 weight percent O_2 in the Ciba 1000 material, may have some unknown effect.

Figure 8 shows another type of nonhomogeneity within the TaC. Figure 9 illustrates an enlarged section and
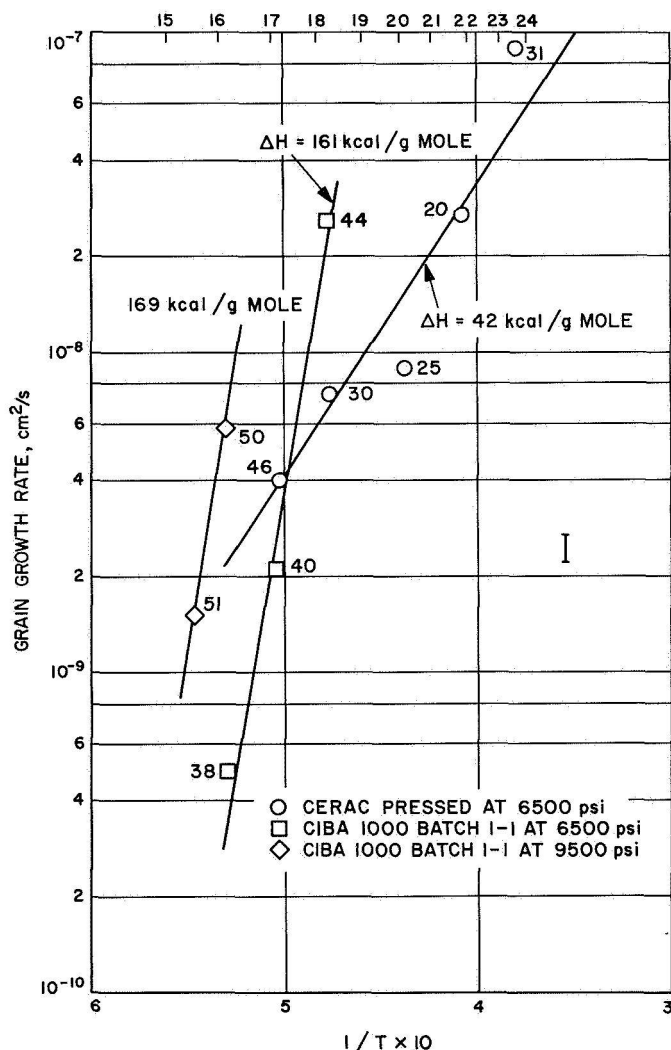

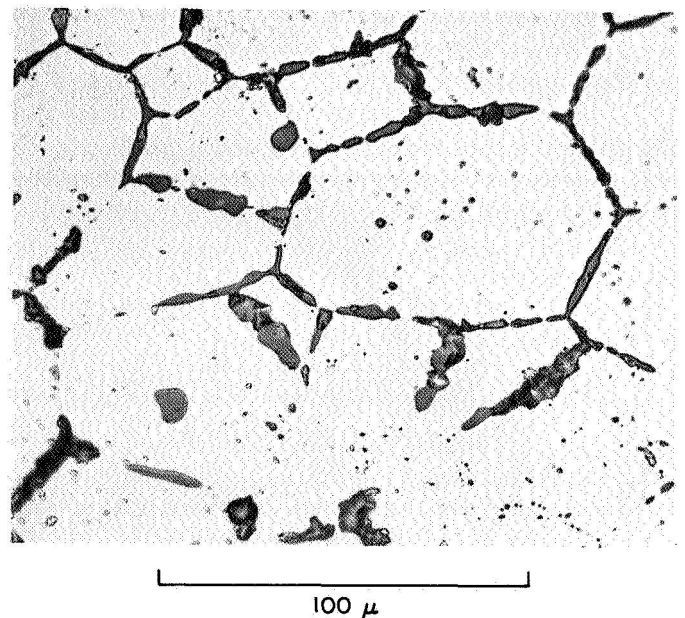Fig. 7. Grain growth rate for tantalum carbide

Fig. 8. Dense tantalum carbide—Ciba 1000 mixture reheated to 2400°C (actual) in vacuum. Electron beam microprobe shows dark areas to be Ta_2O_5
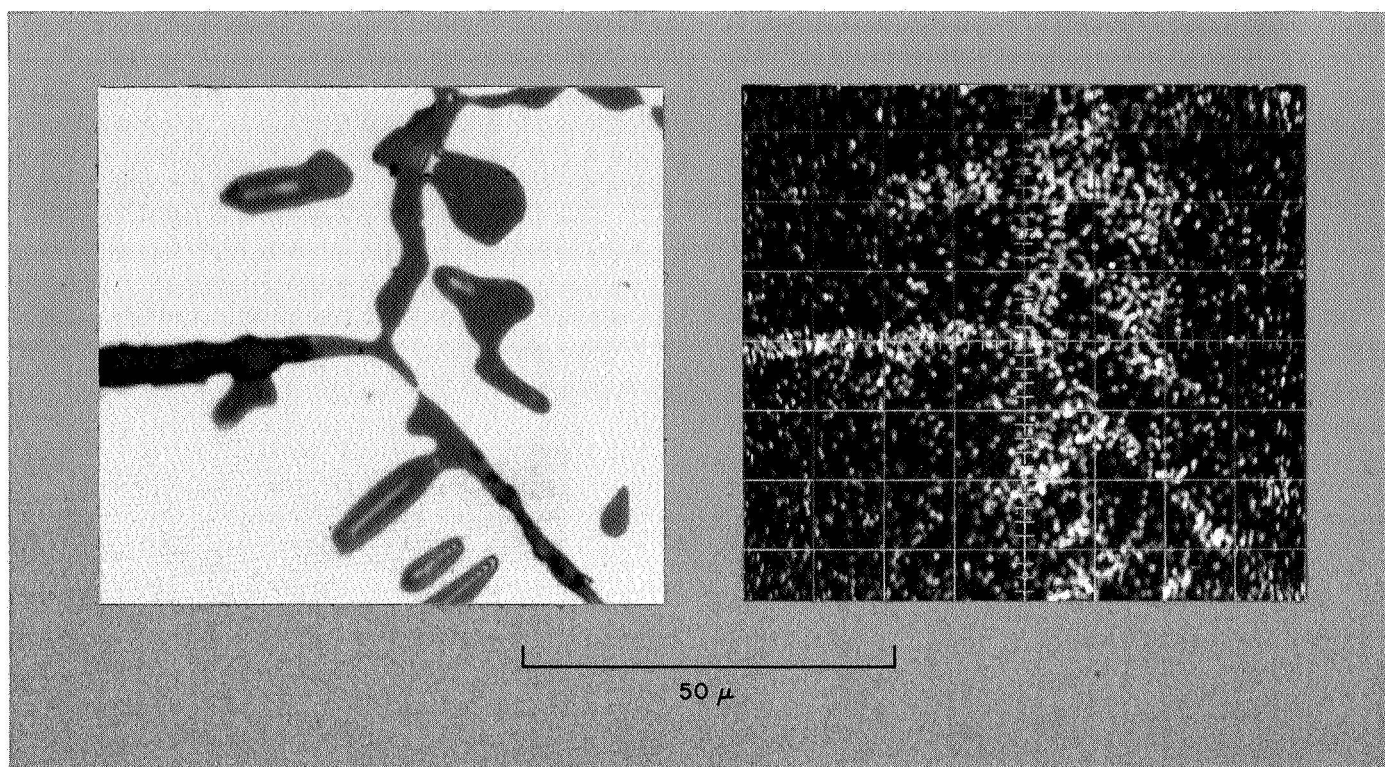
Fig. 9. Enlarged area of Fig. 8 and O₂ Kα (third order) distribution

O₂ distribution (Kα third order). The second phase present at the grain boundary in this sample is tantalum pentoxide as determined by the microprobe when standardized against a sample of pure tantalum pentoxide. In the bulk analyses of the powders from which this material was made, sufficient oxygen is present to account for such concentrations. It is not known whether the distribution of oxygen is nonuniform in the powder and, therefore, this area may represent a local high concentration, or whether relatively uniform distribution of oxygen was concentrated during subsequent hot-pressing and reheating.

D. Conclusions

In spite of the lack of explanation for some of the data observed in this study, the following conclusions may be drawn:

(1) TaC may be fabricated by conventional hot-pressing into dense polycrystalline compacts suitable for experimental purposes. The variables that control the ease of compaction are not completely known, and wide ranges of behavior were observed among similar materials.

(2) The compaction of TaC is apparently not a diffusion-controlled process, and there is slight evidence to support a deformation process.

(3) Careful studies are needed to delineate the role of oxygen in the behavior of TaC.

(4) Problems exist with analytical procedures in TaC.

(5) TaC appears to behave like oxide ceramics in that composition and impurity distribution vary from part to part within a given specimen.

(6) A grain boundary phase of essentially Ta_2O_5 was noted in some reheated TaC.

(7) Activation energies for grain growth were approximately 165 kcal/g mole for Ciba 1000 TaC and 42 kcal/g mole for Cerac TaC. The difference could not be explained.

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